Commercialization of Chromium-Tungsten Alloy Steel for the Petrochemical and Power Industries

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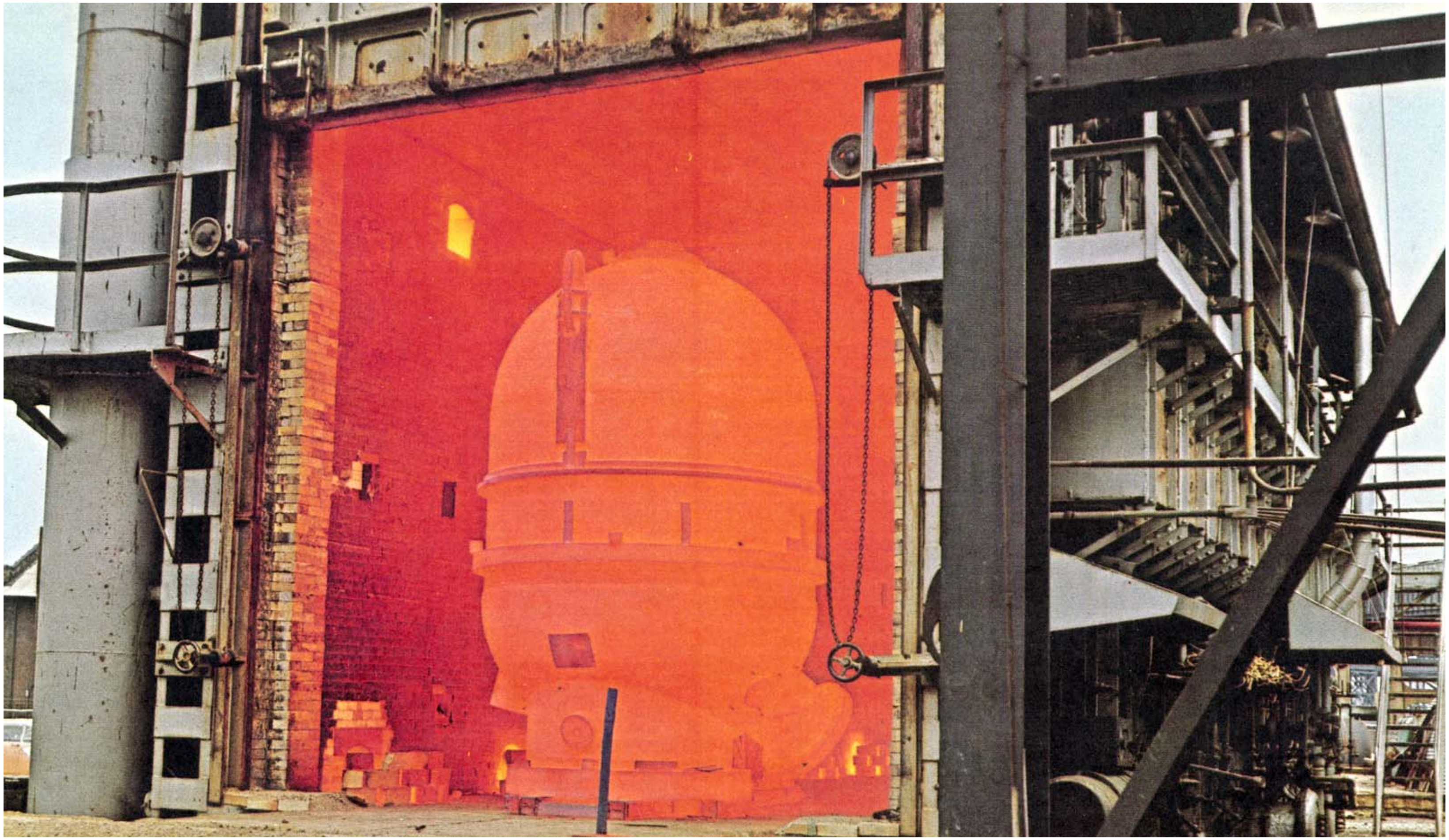
Presently, Vessels Operating at Temperatures Above 900F are Made of 2.25Cr-1Mo Steels. These Vessels Tend to be Large in Diameter Similar to the Vessel

- **2.25Cr-1Mo Vessels Generally Require Postweld Heat Treating (PWHT) in All Thicknesses.**
- **PWHT Increases the Manufacturing Cost and Makes Repairs in the Field More Difficult than Plain Carbon Steel.**
- **One of the Goals of the U.S. DOE is to Minimize Natural Gas Consumption, Whenever Possible, Since Natural Gas is Considered a "Limited Resource" Material.**

Postweld Heat Treating uses Large Quantities of Natural Gas



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- At Present, There is No Activity in the U.S. to Produce Thick Sections of 2.25Cr-1Mo Products such as Plates and Forgings. Also, There is No Activity in the U.S. to Fabricate Large Equipment Made of 2.25Cr-1Mo Steel.
- One Reason for this Lack of Activity is that Equipment can be Purchased at a Lower Price from Foreign Sources.
- In Order to Reverse this Trend as well as Save Energy, an Effort is being Undertaken by DOE, in Conjunction with Nooter Corporation, ORNL (as well as Other Industrial Partners) to Develop a New Steel Material for Elevated Temperature Applications such as Cat Crackers.

Development of a New Steel Material for Elevated Temperature Applications such as Cat Crackers

DOE Project Partners

- The Industrial Partners Consist of a Cross-Section of Interested U.S. Industries
  - Lukens Steel (plate products)
  - National Forge (forged products)
  - Plymouth Tube (pipes and tubes)
  - Ellwood Forge (material producer)
  - ExxonMobil (refiner)
  - BP Amoco (refiner)
  - DuPont (chemicals)
  - Stoody Co. (weld wire)
  - Nooter Eriksen (boiler manufacturer)

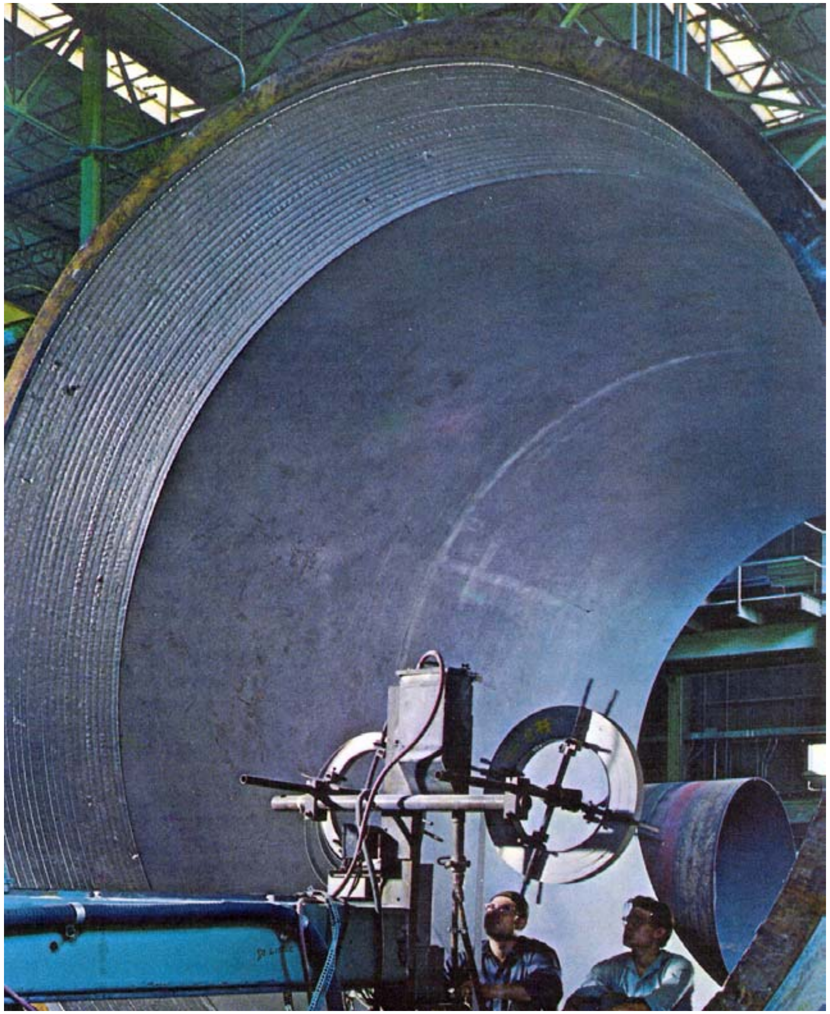
Cr-W Alloy Steel has Attractive Properties

- The New Material has Essentially Two Properties that make it very Attractive to use at Elevated Temperatures.
  - High tensile, yield, creep, and fatigue properties as compared to 2.25Cr-1Mo
  - Possible reduction or elimination of the requirement for PWHT
- Dr. Vinod Sikka will Elaborate on These Properties Later.

(Continued)

- The Properties are also of Interest to the Industrial Partners with Fabrication Capability.
  - Reason is that the material is patented by ORNL and the material partners in the U.S. will be given exclusive license to produce and sell the material worldwide.
- The Properties are of Interest to DOE due to Conservation of Natural Gas and Reduction of Tonnage of Steel due to its Greater Strength.

Weld Overlaying of a Large Pressure Vessel



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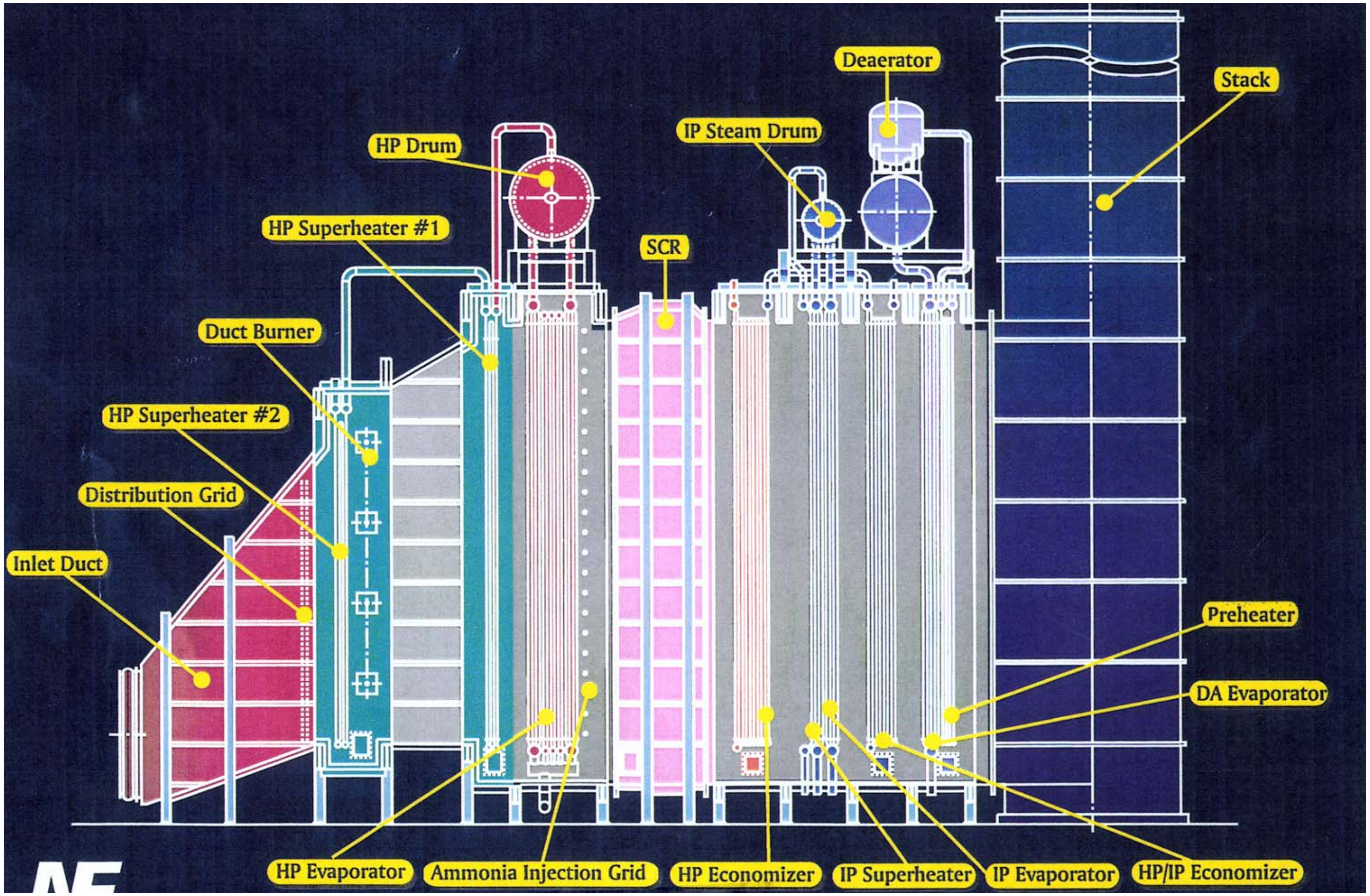
- **This Arrangement will Ensure that the Material Production and Fabrication will Remain in the U.S. for the Foreseeable Future.**
- **This New Steel Material will be Designated as Alloy 33 with a Composition of 3Cr-3W as well as Other Alloying Elements. It will be Used in Pressure Vessels as well as Boilers.**

Alloy 33 will be used in Pressure Vessels as well as Boilers



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- Initial Tests on Non-welded Material Show Excellent Results. Data is Presently being Generated to Submit to the ASME Code for Approval.
- Tests are Currently Under Way for the Welded Material. Both Submerged Arc Welding (SAW) and Gas Tungsten Arc Welding (GTAW) are being Investigated.
- The Possible Elimination of PWHT Makes this Material Viable for Vessels that Need Field Repairs such as Coke Drums.

Coke Drum

Development of a New Class of Fe-3Cr-W(V) Ferritic Steels for Industrial Process Applications

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and

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Ron Klueh

Phil Maziasz

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Mike Santella

IMF Review Meeting

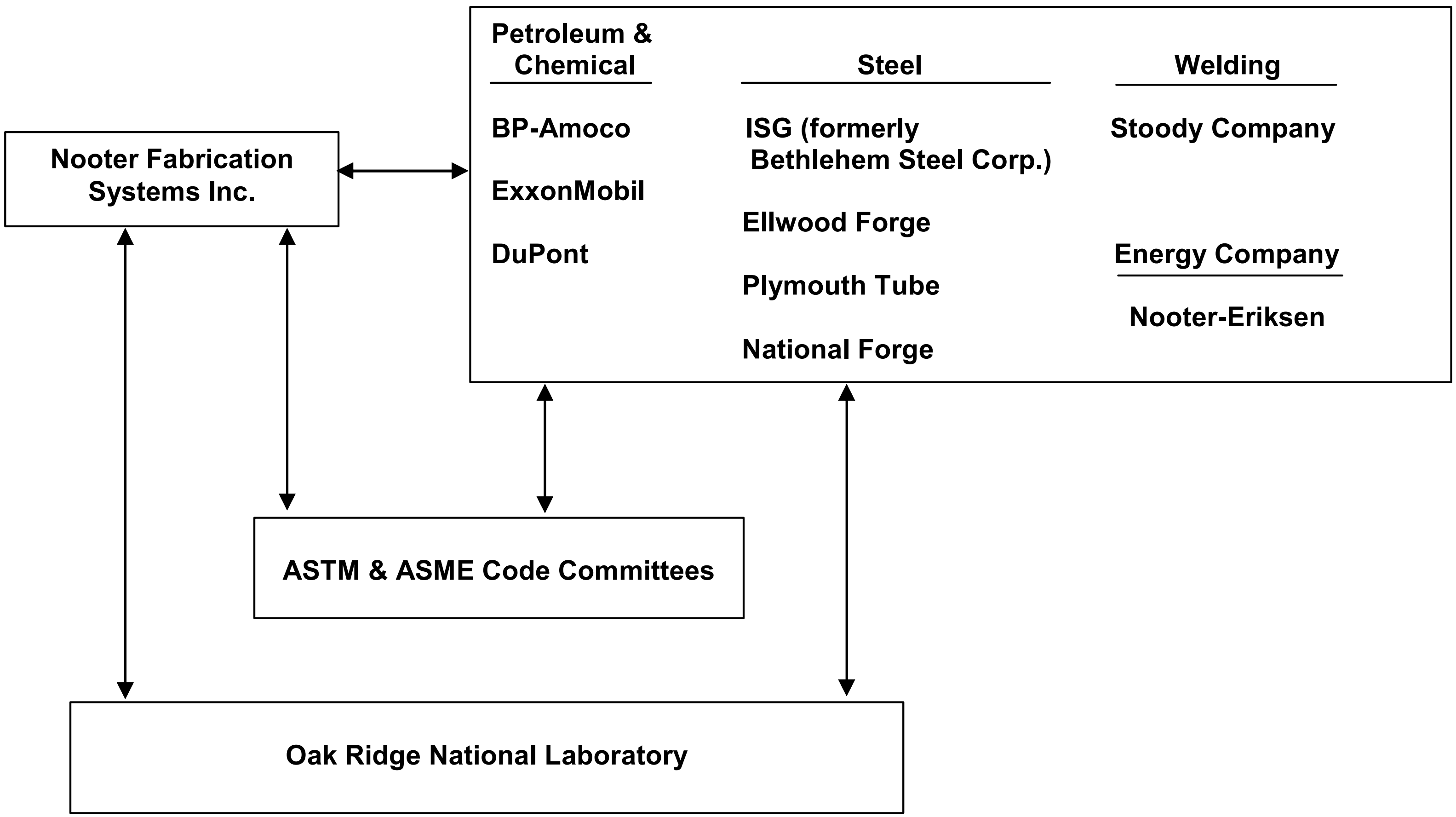
Golden, CO

June 24, 2003

Project Objective

- Develop New Class of Fe-3Cr-W(V) Ferritic Steel with
  - 50% higher tensile and creep strength than the current high-strength modifications of 2.25Cr-1Mo steel (T23)
  - Lower DBTT and higher upper-shelf energy
  - Ease of heat treating
  - With strong potential for not requiring PWHT after welding

The Project is a Multiple IOF Industry Partnership



Use of Fe-3Cr-W(V) Alloys will Result in ~ 21 Trillion Btu/year of Energy Saving and ~ $237 Million/Year in Cost Savings for Chemical and Related Components

- Reduced Section Thickness by 30 to 50%
- Larger Number of Fabrication Processes Requiring Less Energy Possible with Reduced Section Thickness
- Less Weld Metal and Welding Time Needed
- Strong Potential for not Requiring PWHT
- If Required, Postweld Heat Treatment Cycle will be Shorter for Thinner Sections
- Overall Weight of Fabricated Component Reduced by 30 to 50%

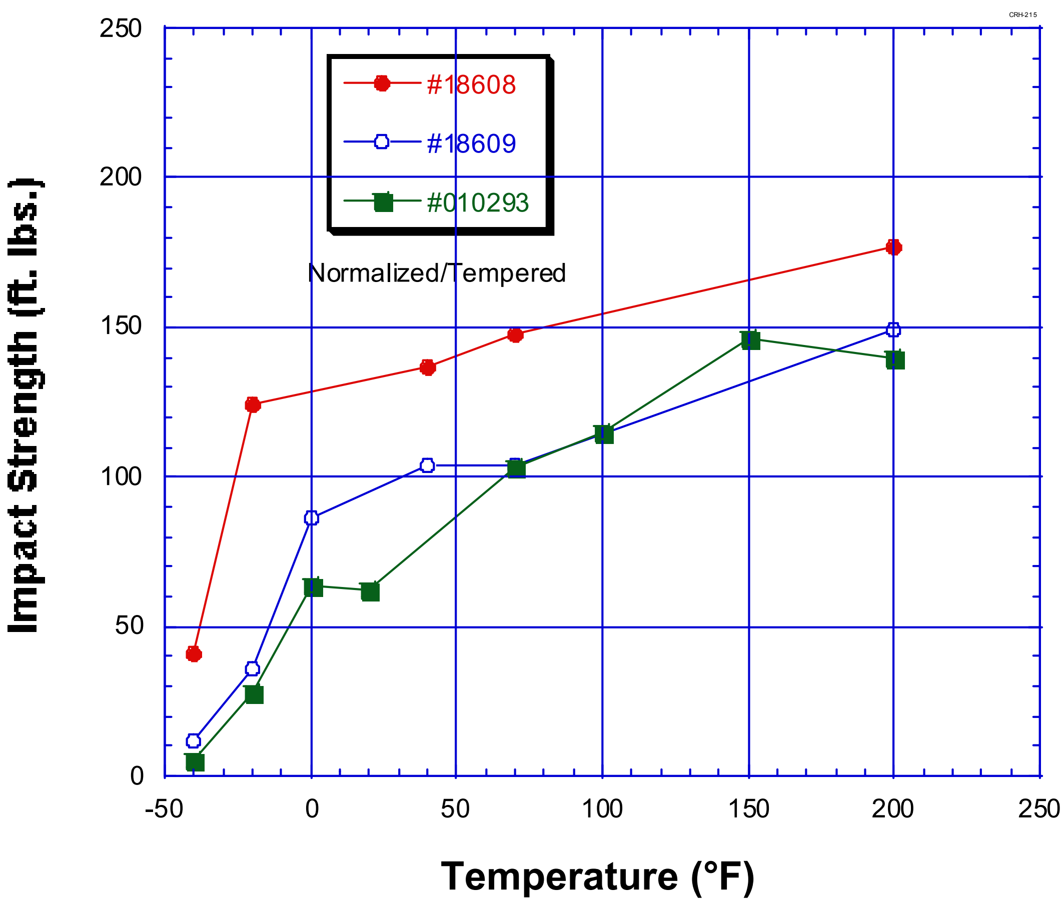
Project's Progress

- **Experimental Heat Melting and Processing for Mechanical Properties**
  - Compositional effects
  - Heat treatment effects
- **Welding Process and Filler Wire Development with Focus on not Requiring PWHT**
  - GTA
  - SA
- **Modeling in Support of**
  - Microstructures after heat treatment
  - Filler wire composition and PWHT effects on impact properties

Project's Progress (Continued)

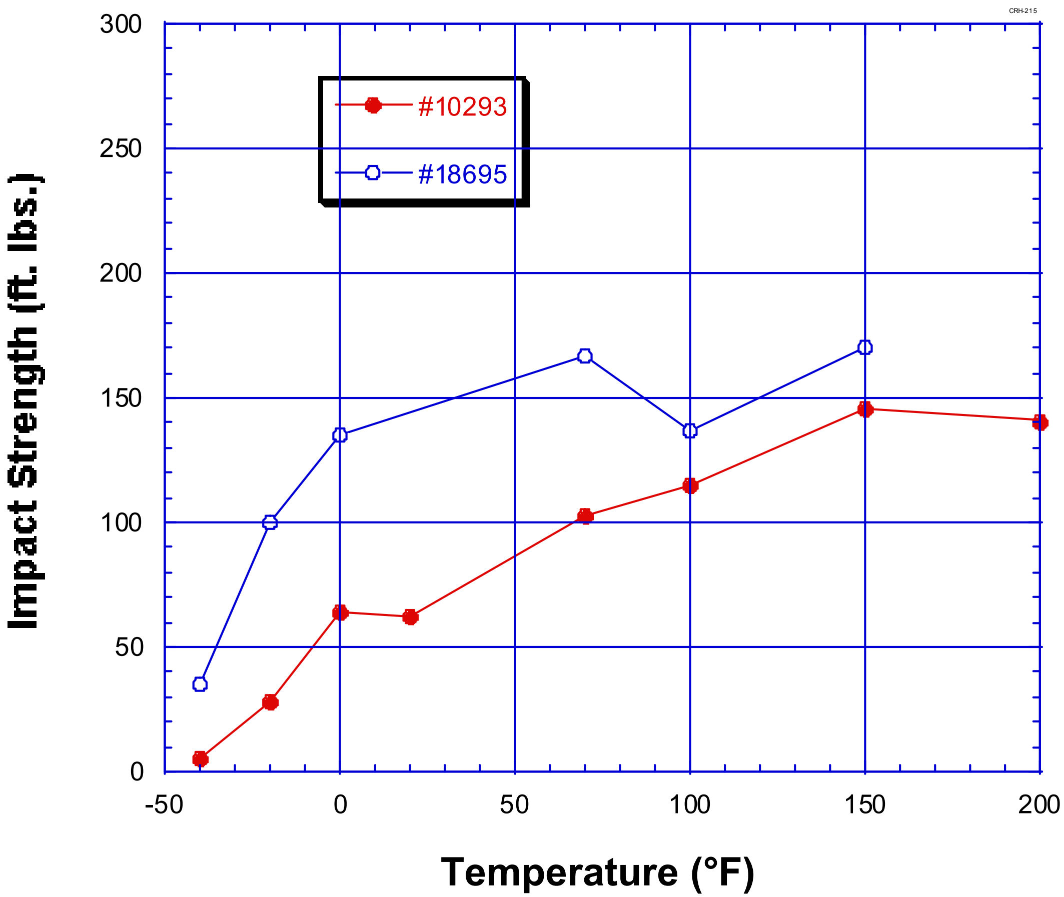
- Microstructural Analysis in Support of
  - Phase stability under creep conditions
  - Weld microstructures
- Scale-up of Pilot Size Heats
  - Melting and processing experience
  - Properties
- Plans for Commercial Heats for ASTM and ASME Code Data

Data Shows that W in Fe-3Cr Alloy is Replaceable by W + Mo



Chemical Composition			
	#18608	#18609	#010293
Carbon	0.075	0.14	0.10
Manganese	0.24	0.480	0.39
Phosphorus	0.006	0.007	0.01
Sulfur	0.01	0.005	0.004
Silicon	0.21	0.21	0.16
Nickel	<0.01	<0.01	0.01
Chromium	3.01	3.02	3.04
Molybdenum	0.75	0.76	0.01
Vanadium	0.24	0.24	0.21
Columbium	0.001	0.002	0.003
Titanium	0.003	0.003	0.001
Cobalt	0.007	0.006	0.005
Copper	<0.01	<0.01	0.01
Alumnium	0.004	0.004	0.003
Boron	0.001	<0.001	0.001
Tungsten	1.54	1.52	3.05
Arsenic	0.002	0.001	0.001
Tin	0.003	0.002	0.003
Zirconium	<0.001	0.001	0.001
Nitrogen	<0.001	<0.001	0.004
Oxygen	0.001	0.004	0.005
Tantalum	<0.01	<0.01	

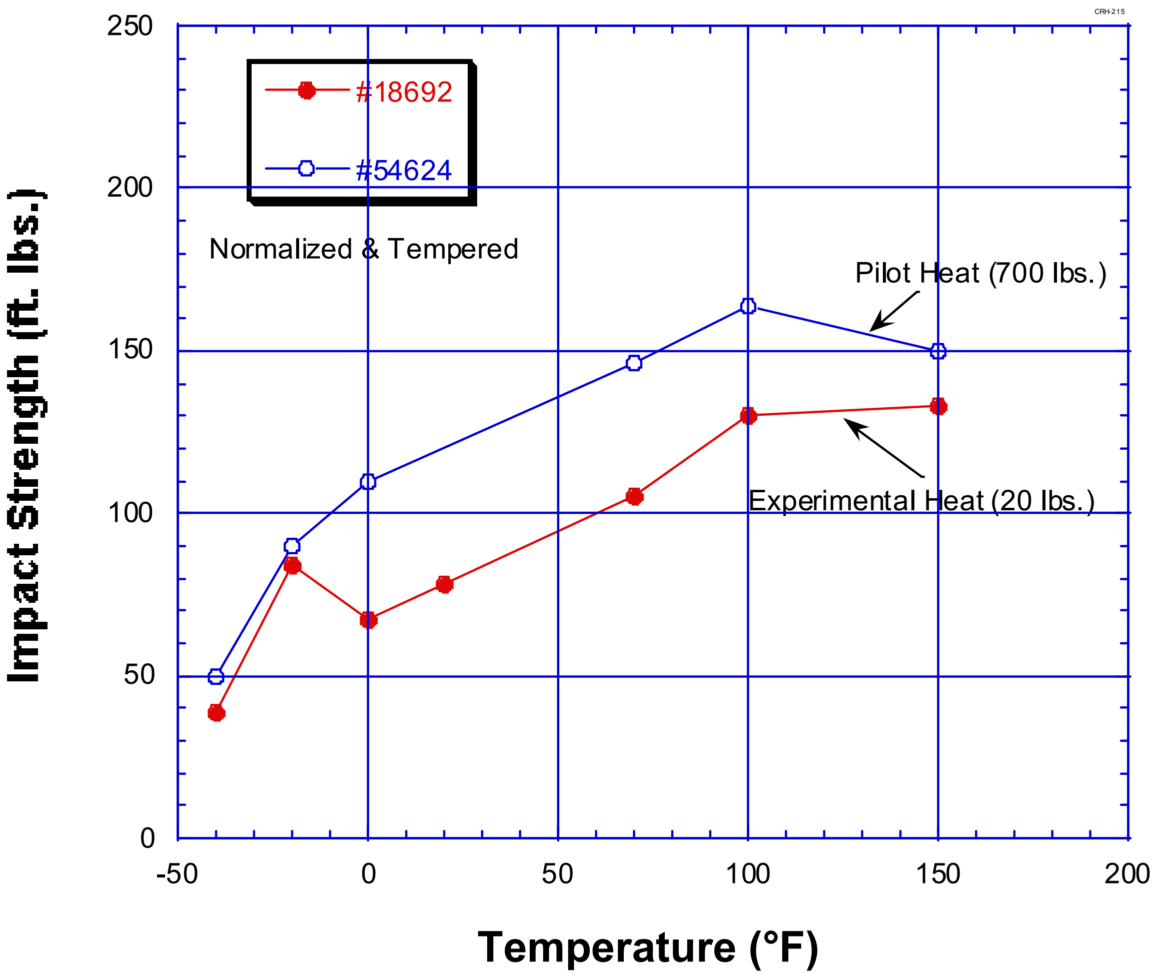
Data Shows Beneficial Effect of Adding 0.5% Ni on Impact Properties

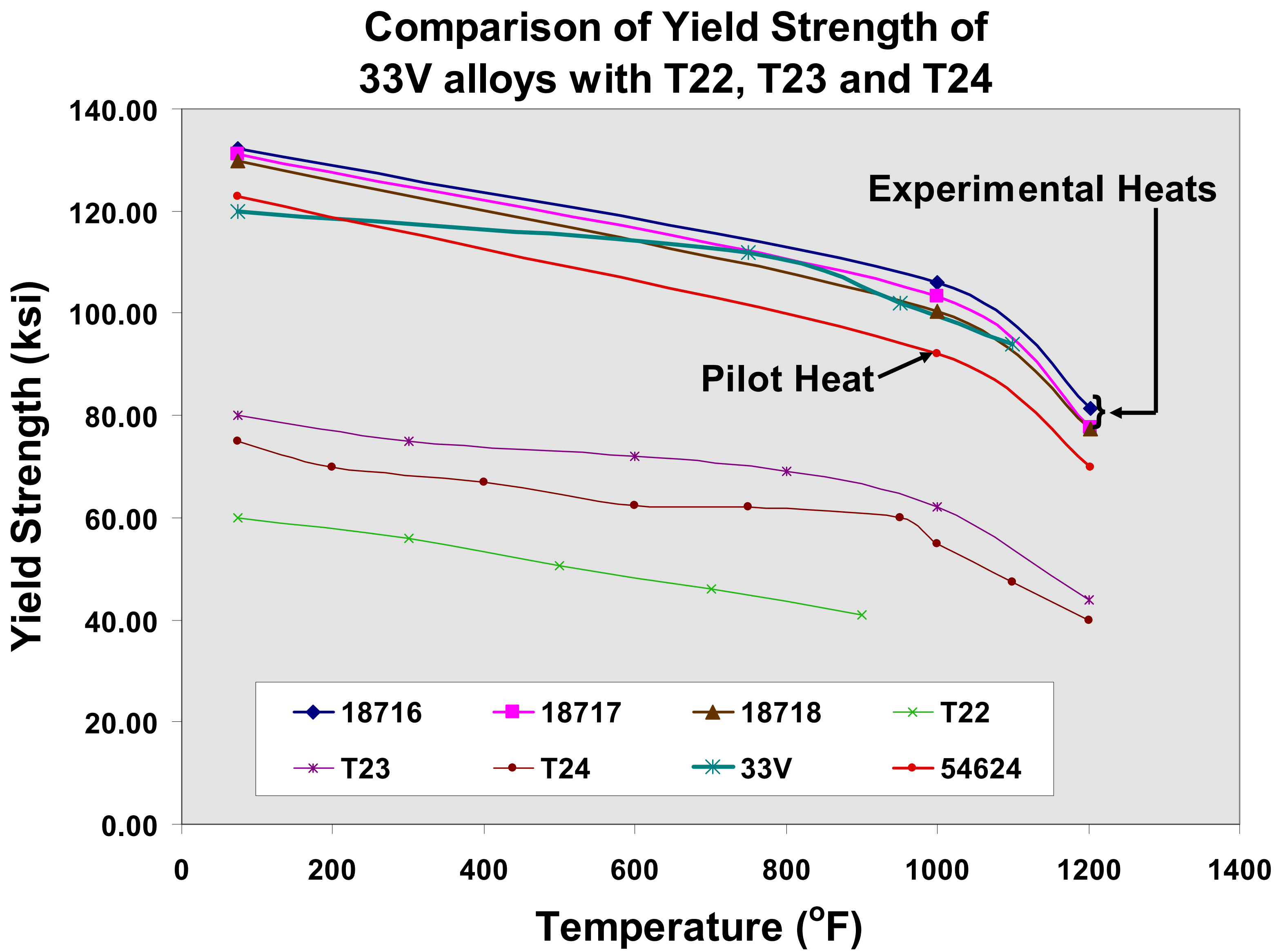


Chemical Composition

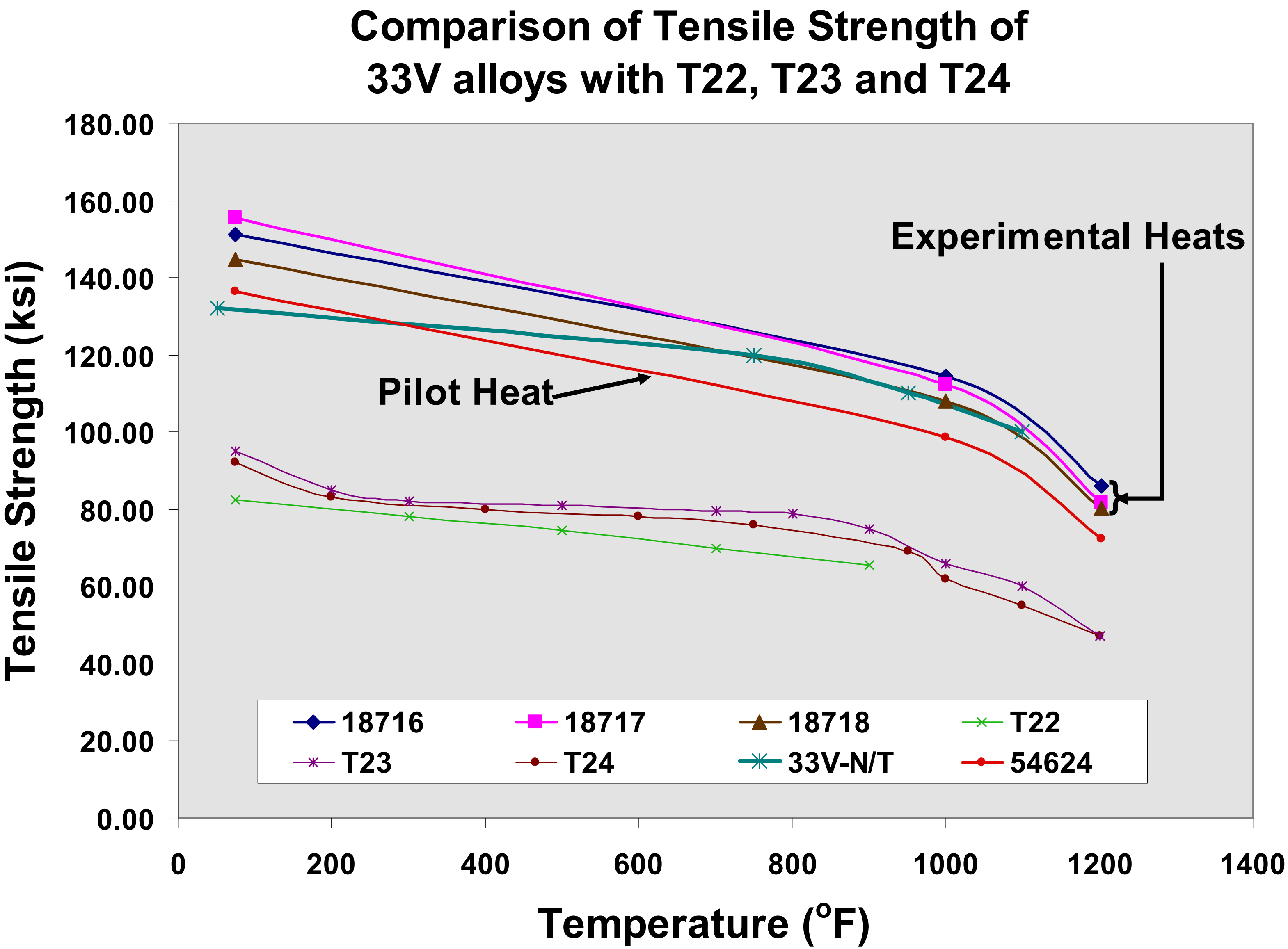
	#010293	#18695
Carbon	0.10	0.095
Manganese	0.39	0.33
Phosphorus	0.01	0.008
Sulfur	0.004	0.006
Silicon	0.16	0.20
Nickel	0.01	0.50
Chromium	3.04	3.03
Molybdenum	0.01	0.74
Vanadium	0.21	0.23
Columbium	0.003	0.002
Titanium	0.001	0.003
Cobalt	0.005	0.006
Copper	0.01	0.01
Alumnium	0.003	0.002
Boron	0.001	<0.001
Tungsten	3.05	1.54
Arsenic	0.001	0.002
Tin	0.003	0.002
Zirconium	0.001	0.001
Nitrogen	0.004	<0.001
Oxygen	0.005	0.001

Pilot Heat Showed Impact Properties Similar to Those for Experimental Heats

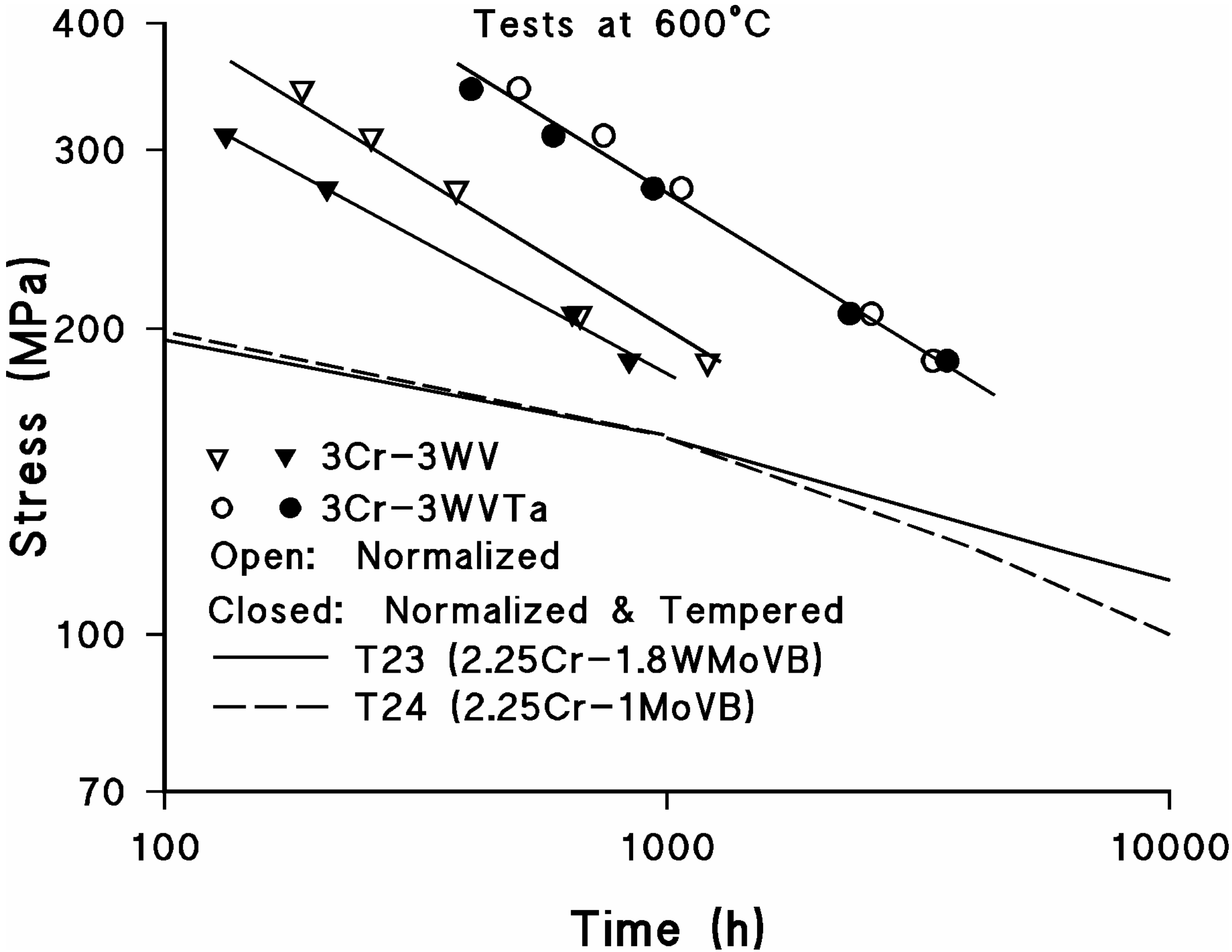


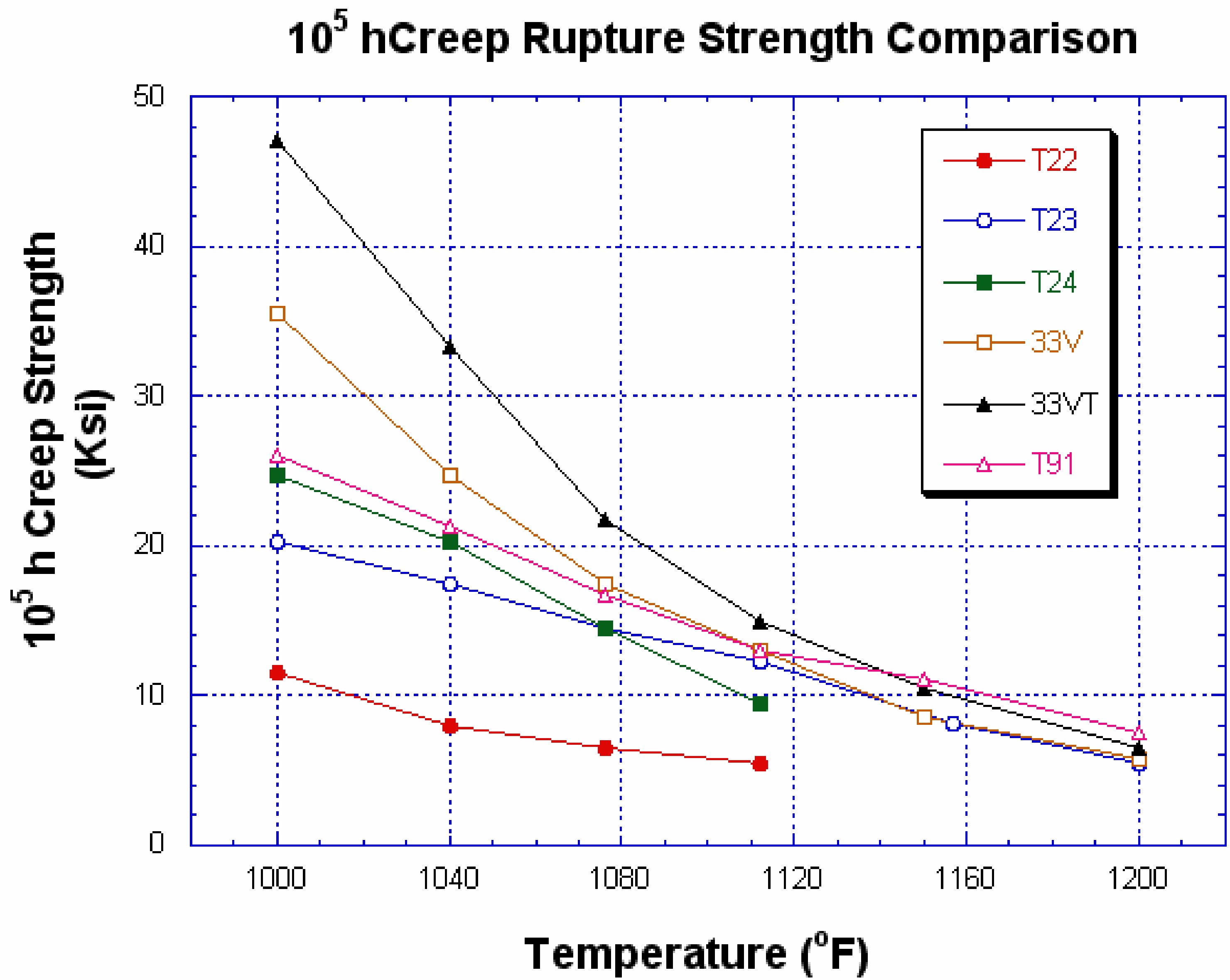


Comparison of Yield Strength of
33V alloys with T22, T23 and T24
Experimental Heats
Pilot Heat
Yield Strength (ksi)
140.00
120.00
100.00
80.00
60.00
40.00
20.00
0.00
0
200
400
600
800
1000
1200
1400
Temperature (°F)
18716
18717
18718
T22
T23
T24
33V
54624


Comparison of Tensile Strength of
33V alloys with T22, T23 and T24
Experimental Heats
Pilot Heat
Tensile Strength (ksi)
Temperature (°F)
180.00
160.00
140.00
120.00
100.00
80.00
60.00
40.00
20.00
0.00
0
200
400
600
800
1000
1200
1400
18716
18717
18718
T22
T23
T24
33V-N/T
54624

Comparison with T23 and T24

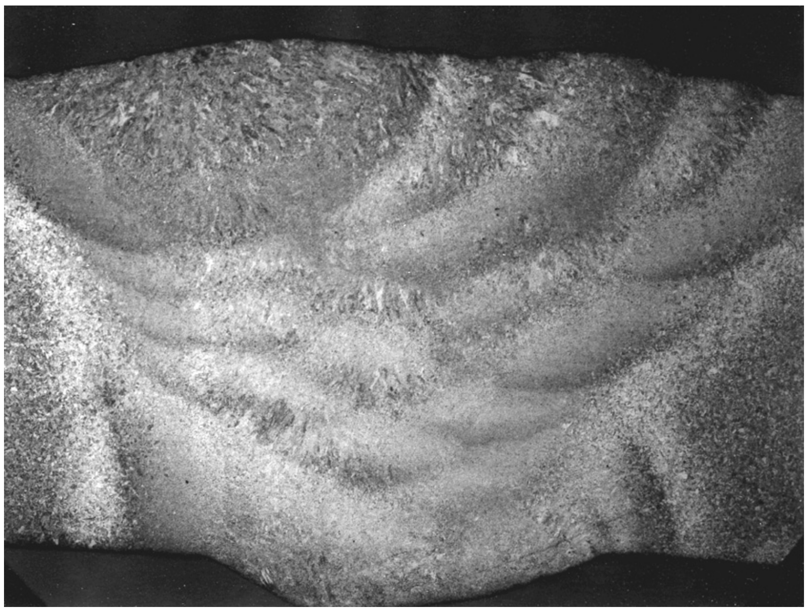




10^5 hCreep Rupture Strength Comparison
10^5 h Creep Strength (Ksi)
Temperature (°F)
T22
T23
T24
33V
33VT
T91
0
10
20
30
40
50
1000
1040
1080
1120
1160
1200

SA Weld has Significantly Less Number of Passes than GTA Weld

13 Passes



02-3667-01 GTA

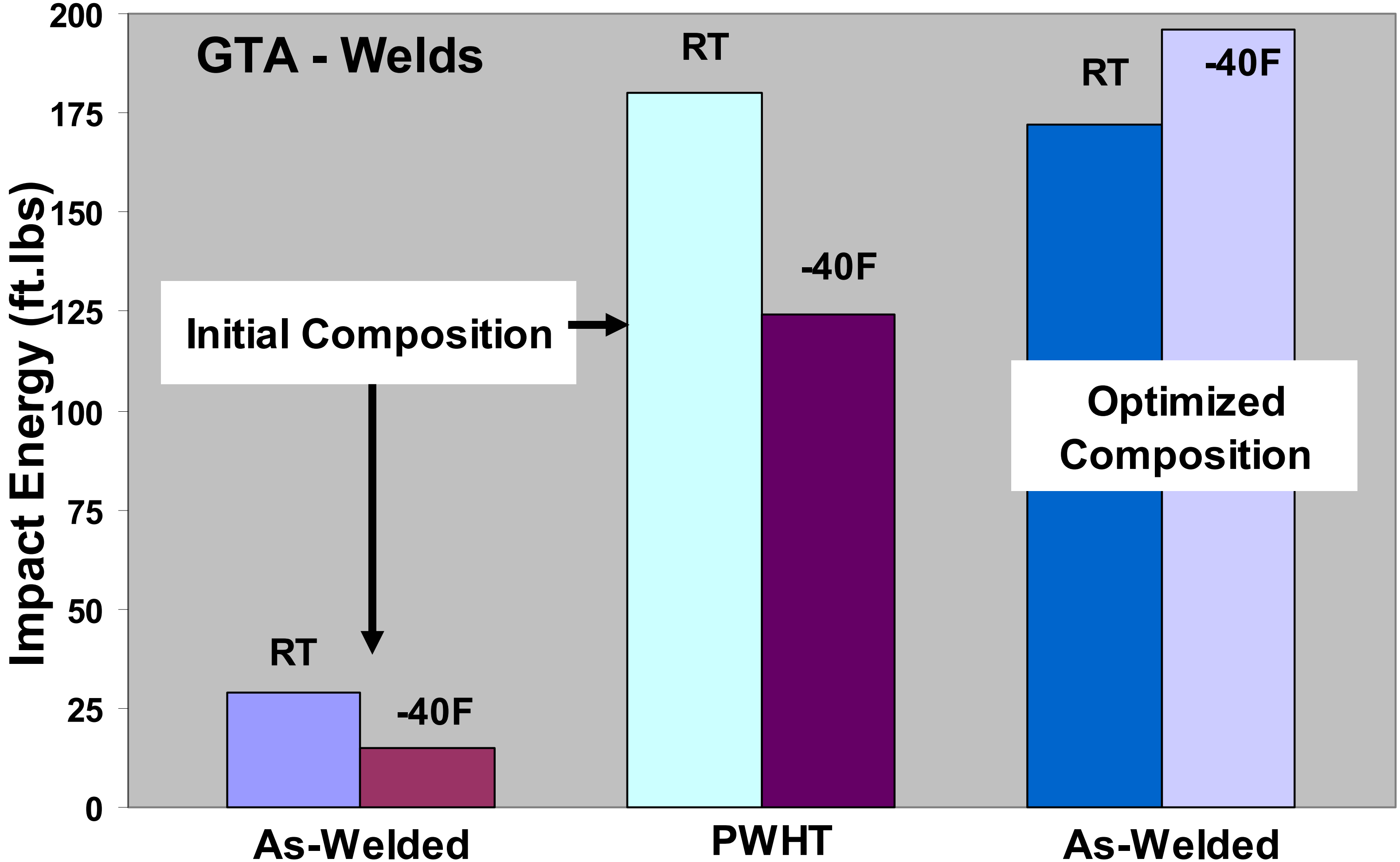
4 Passes

02-3652-01 SA

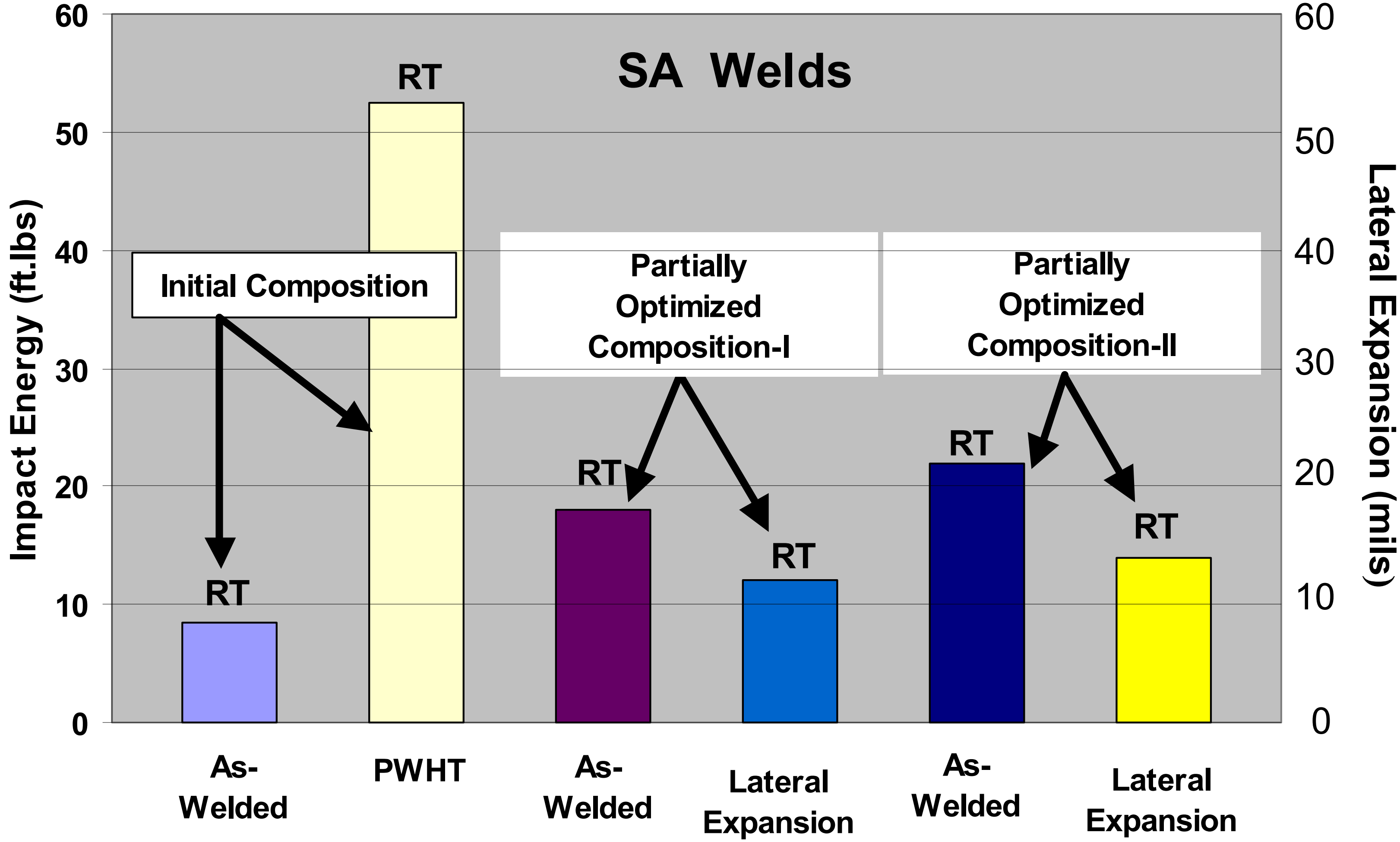
2mm

Vilella's Reagent

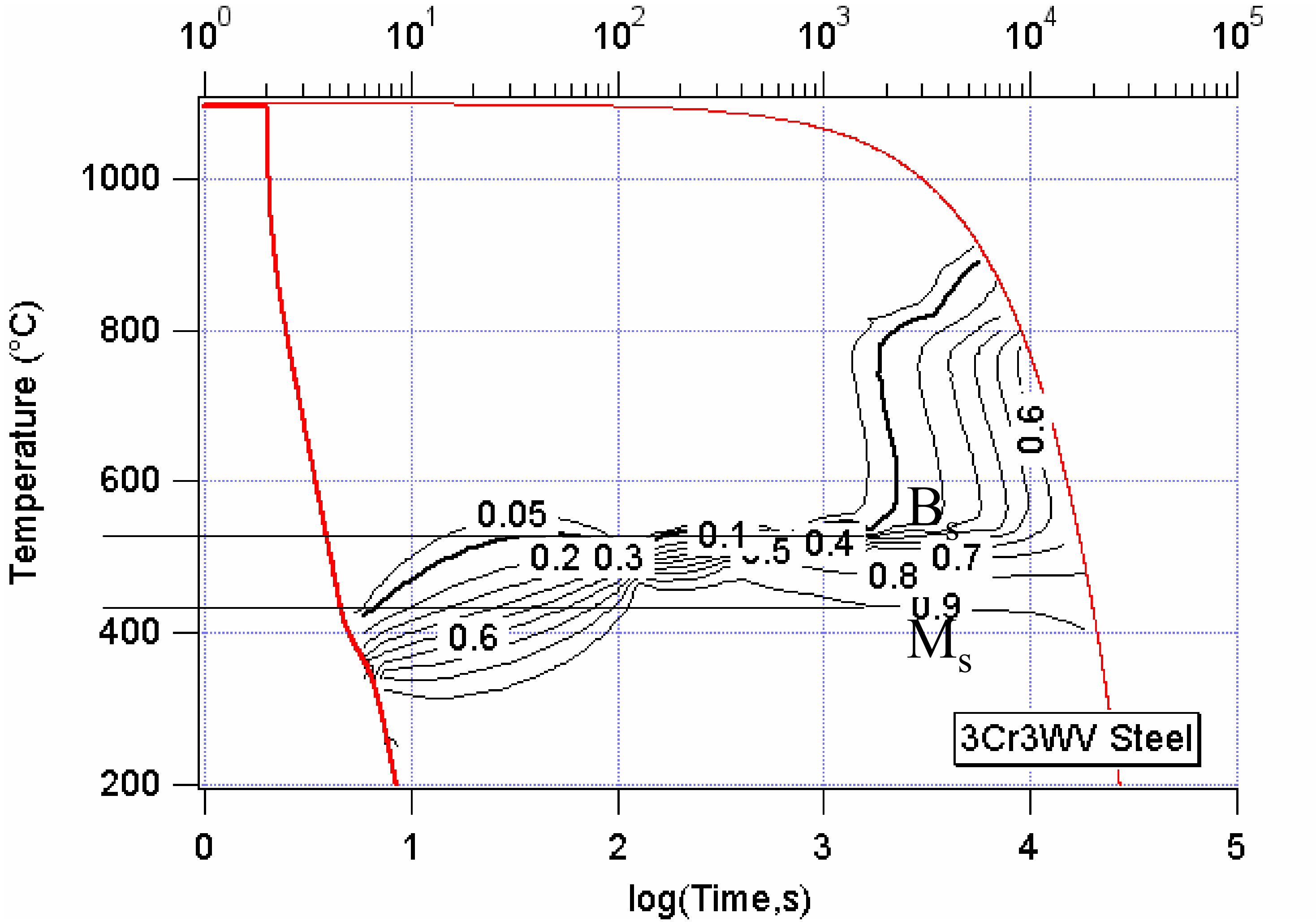
GTA filler wire composition is optimized



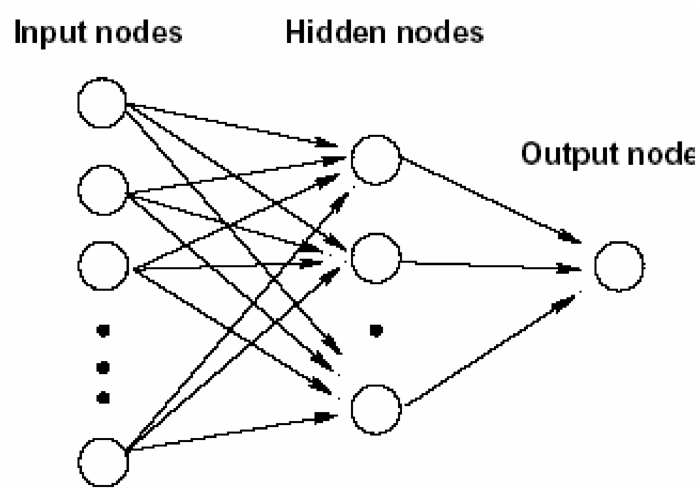
SA filler wire composition is still being optimized

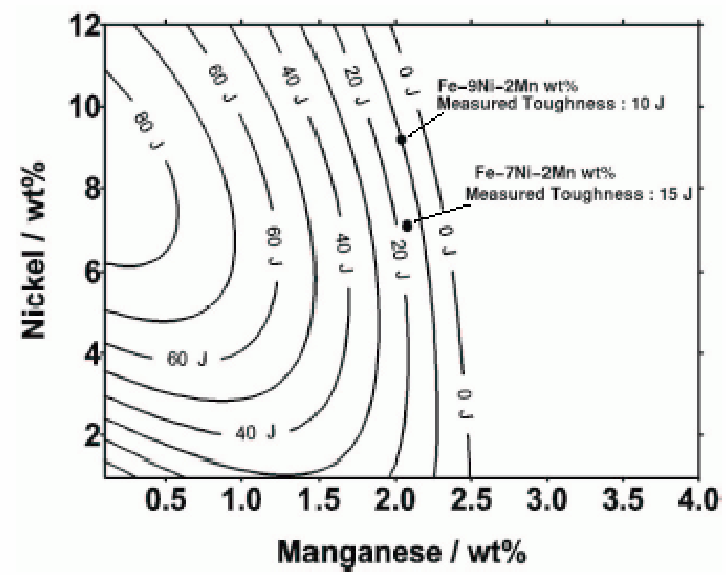


Measured CCT diagram and cooling rate effect



A comprehensive neural network to predict YS, TS, Ductility and toughness of shielded metal arc weld deposits developed in University of Cambridge, UK was used to optimize filler metal compositions for SA Welds.



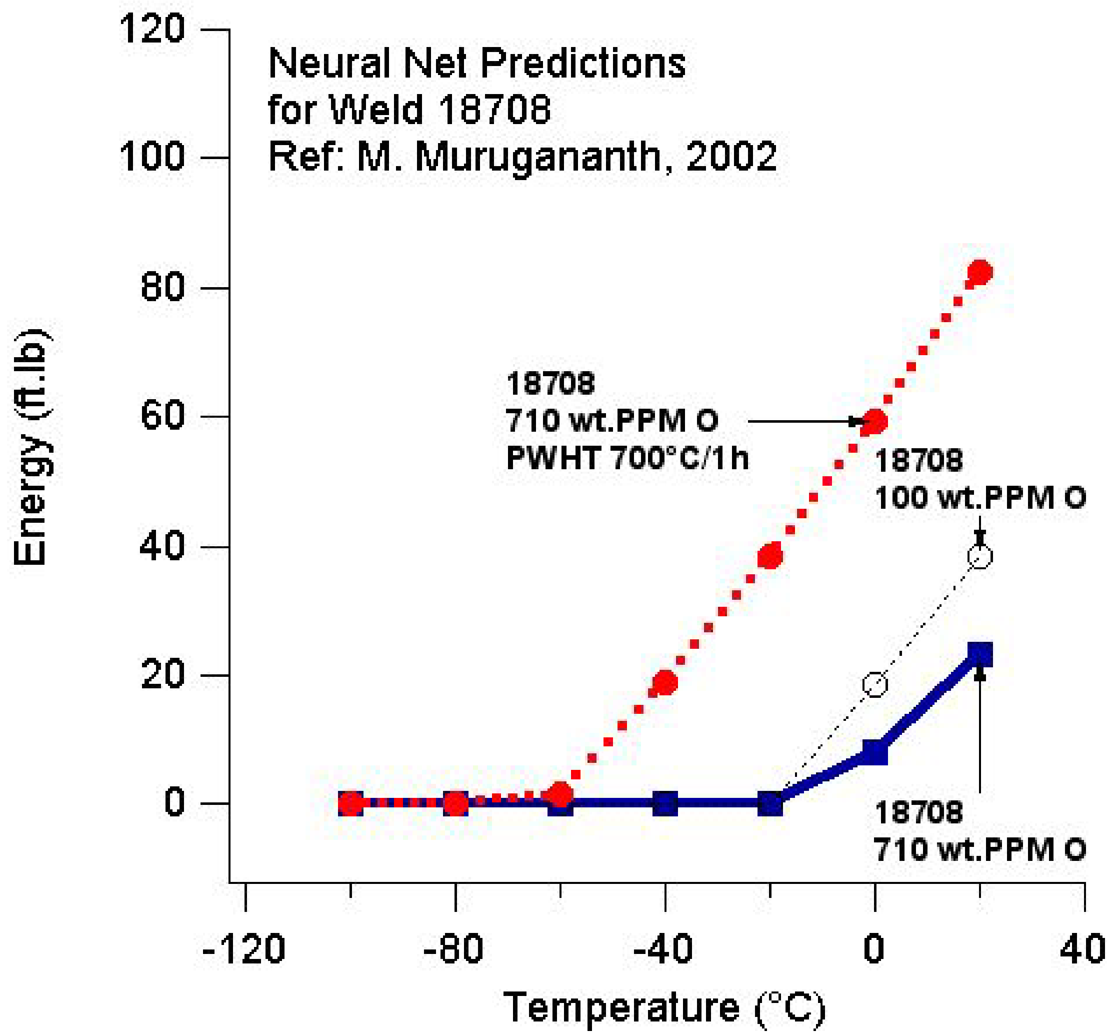


- The model considers alloying element (C, Si, Mn, Ni, Mo, Cr, W, Co, Ti, O, and N) interpass temperature, heat input, and post weld heat treatment conditions.

Changes in Weld Deposit Chemistry between GTA and SA Weld for Same Filler Wire (18687) and 880 Flux

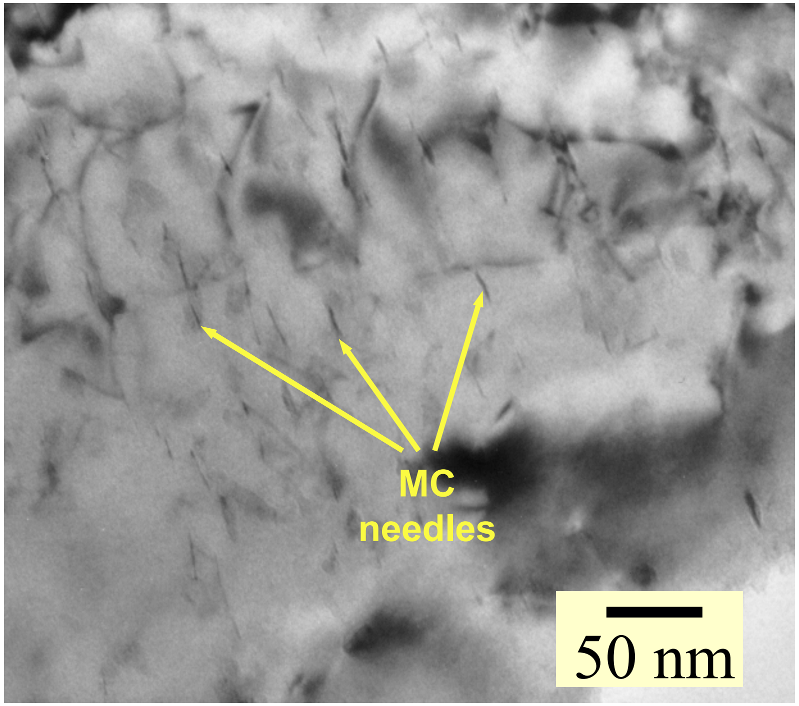
Element	Wt (%)		
	Wire	GTA Deposit Argon Cover Gas	SA Deposit 880 Flux
C	0.070	0.052	0.047
Mn	0.20	0.20	0.15
Si	0.21	0.24	0.25
V	0.25	0.25	0.22
N	0.001	<0.001	**0.004**
O	0.003	0.002	**0.044**

Predicted Charpy toughness curves for weld composition based on Weld 18708.

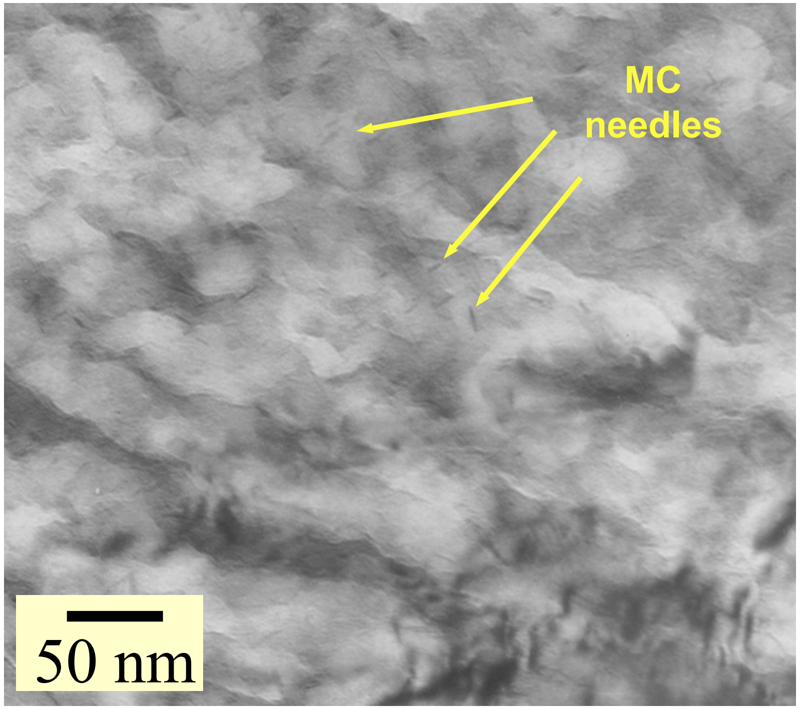


Uniform dispersions of Ultra-fine V-rich MC needles are present in both 3Cr–3WV and 3Cr–3WVTa after Normalizing at 1100°C and tempering at 700°C

TEM (foil) 3Cr–3WV (N+T)

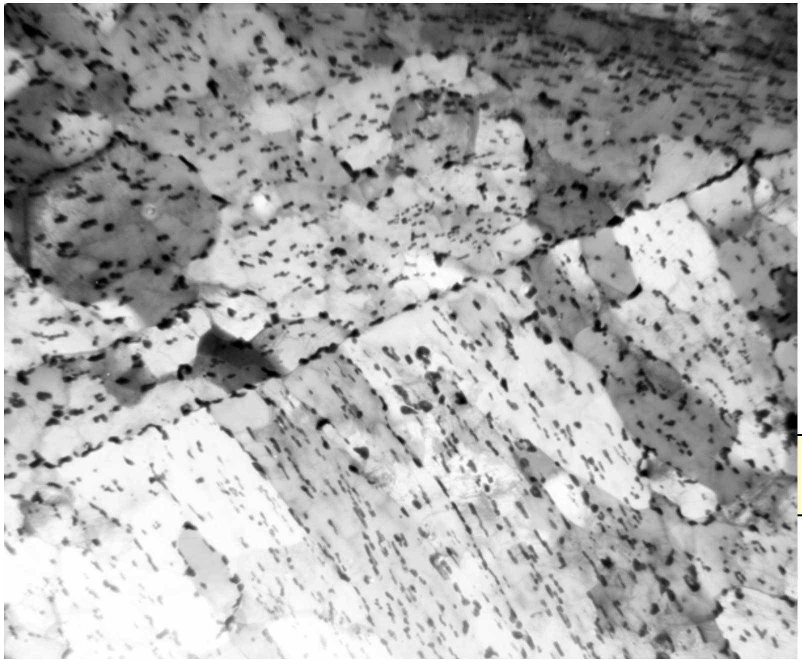


TEM (foil) 3Cr–3WVTa (N+T)

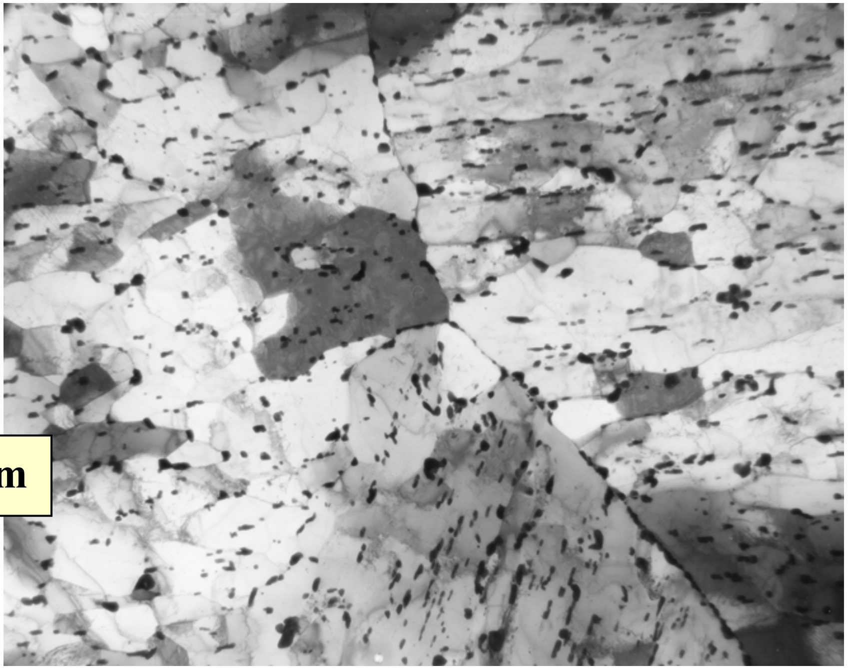


Better Creep Resistance of 3Cr-3WVTa Steel is due to Finer Dispersion of MC Carbides Remaining Within Sub grains

(TEM of creep tested gage)



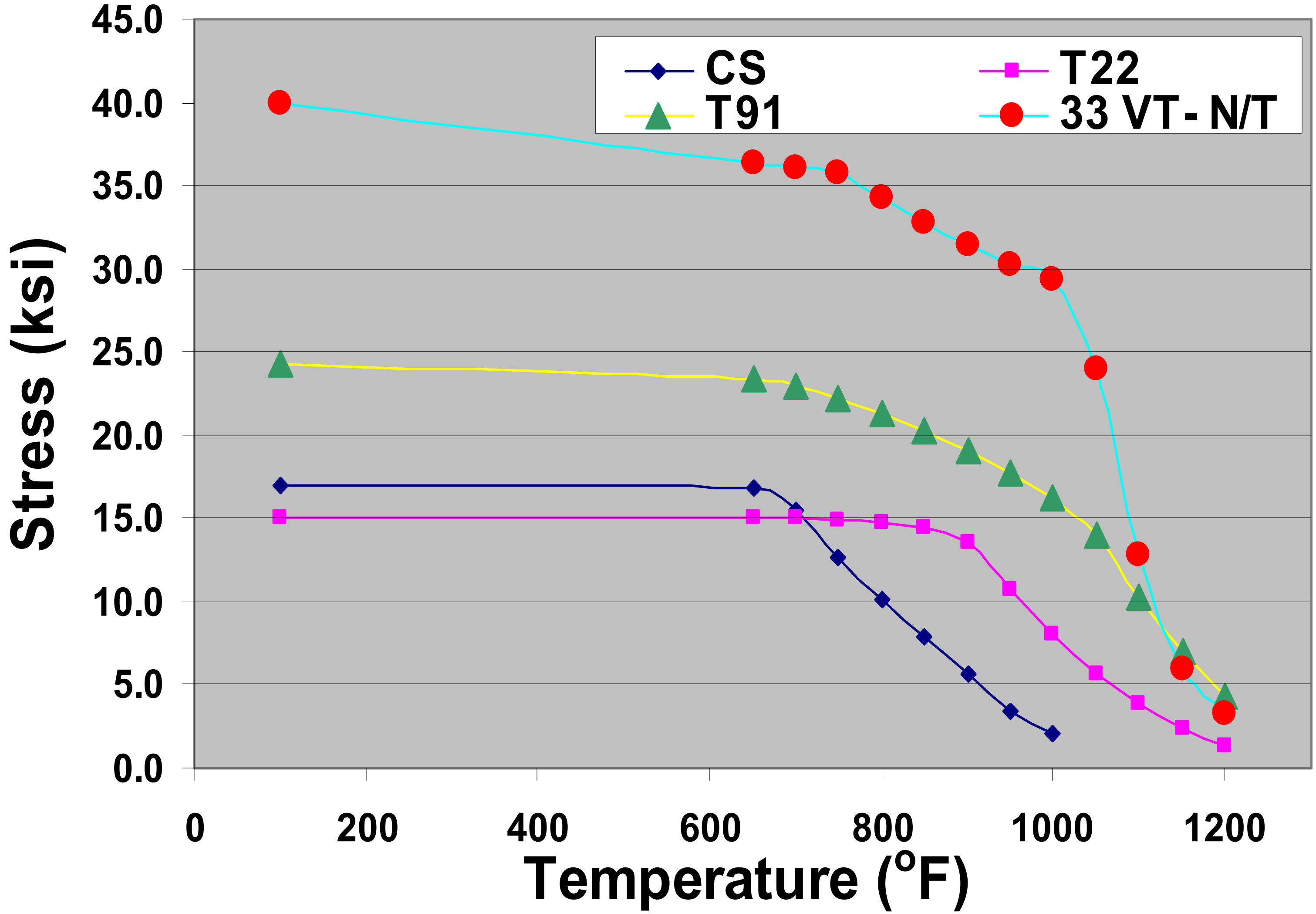
5 μm



3Cr-3WV (N+T)
Creep at 12 ksi/650°C
t_r = 1141h

3Cr-3WVTa (N+T)
Creep at 12 ksi/650°C
t_r = 3086h

Allowable Design Stress values



Plans for Commercial Heats for ASTM and ASME Code Data

- Need Data on Three Commercial Size Heats
- Plans to get Three Commercial Size Heats
  - Melt 40-Ton Heat by vacuum degassing process
  - Cast into
    - One slab ingot for rolling into plate
    - One round ingot for forging into billet and product form
    - Two electrodes
      - One to be re-melted by ESR
      - One to be re-melted by VAR
- Three Heats will Consist of:
  - Vacuum degassed heat
  - ESR heat
  - VAR heat

Summary and Conclusions

- New Base Metal Compositions that Meet the Project Objective have been Identified and a Patent Application was Filed.
- Filler Wire Compositions for GTA Welds that Require no PWHT have been Identified.
- Filler Wire Composition and Flux Type for SA Welds that Require no PWHT have Nearly been Identified but Need Further Improvement to Exceed the Minimum Requirements
- Procurement Order for Commercial Heats has been Placed

Future Work

- Receive Commercial Size Heats and Begin their Characterization
- Continue Further Optimization for Improving SA Weld Properties without PWHT
- Manufacture and Install Prototype Component
- Begin Preparing ASTM and ASME Code Packages

Chemical Composition of Base and Commercial alloys

Element	Alloy (wt %)					
	Commercial / Near Commercial				Current	
	T22[a]	T23*a,c*	T24[a,d]	T9[a,e]	33V[f]	33VT[f]
C	0.15 max	0.04-0.10	0.05-0.10	0.08-0.12	0.1	0.1
Si	0.25-1.00	0.50 max	0.15-0.45	0.20-0.50	0.2	0.2
Mn	0.30-0.60	0.10-0.60	0.30-0.70	0.30-0.60	0.5	0.5
P	0.030 max	0.030 max	0.020 max	0.020 max	0.020 max	0.020 max
S	0.030 max	0.010 max	0.010 max	0.010 max	0.010 max	0.010 max
Cr	1.9-2.6	1.9-2.6	2.2-2.6	**8.0-9.5**	**3**	**3**
Mo	0.87-1.13	0.05-0.30	**0.90-1.10**	**0.85-1.05**	*b*	*b*
N	*b*	0.030 max	0.12 max	0.030-0.070	*b*	*b*
W	*b*	**1.45-1.75**	*b*	*b*	**3**	**3**
V	*b*	**0.20-0.30**	**0.20-0.30**	**0.18-0.25**	**0.25**	**0.25**
Nb	*b*	**0.02-0.08**	*b*	**0.06-0.10**	*b*	*b*
Ta	*b*	*b*	*b*	*b*	*b*	**0.1**
B	*b*	**0.0005-0.0060**	**0.0015-0.0070**	*b*	*b*	*b*
Ti	*b*	*b*	**0.05-0.10**	*b*	*b*	*b*
Ni	*b*	*b*	*b*	0.40 max	*b*	*b*
Al	*b*	0.030 max	0.020 max	0.040 max	*b*	*b*
Fe	*g*	*g*	*g*	*g*	*g*	*g*

a = ASTM A213
b = Not specified
c = *Code Case 2199*
d = Code Case draft
e = Code approved
f = Nominal (range to be specified)
g = Balance